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(54) **Plasto-elastic polypropylene compositions.**

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## Description

This invention refers to thermoplastic polypropylene compositions having elastomeric properties, obtained in the form of spheroidal particles, endowed with specific flowability and apparent density characteristics, and to their preparation method.

During the last few years, polypropylene compositions having elastic properties while maintaining the capability of being transformed into manufactured articles using the same apparatus and process normally used for thermoplastic materials, have gained more and more importance.

Said compositions, sometimes referred to as polyolefin thermoplastic elastomers, have found application above all in the automotive, electric cables and sporting goods fields. Because of their advantageous performances, they tend to replace the more expensive thermoplastic styrene and butadiene based rubbers.

The compositions are prepared by mixing, under dynamic vulcanization conditions, ethylene-propylene rubbers (EPR), or ethylene-propylene-diene rubbers (EPDM), with crystalline polyolefins, in particular polypropylene.

Such a preparation process involves a considerable use of energy and the mechanical homogeneity of the components is not always such to impart the desired balance of optimum properties to the final product.

Therefore, the need is felt to be able to produce polyolefin compositions with the desired balance of elasto-plastic properties through polymerization processes.

A method for the preparation of polymer products having elasto-plastic properties directly in the polymerization phase is described in USP 4,298,721.

The thermoplastic elastomers described in such a patent are obtained by polymerizing ethylene-propylene mixtures using specific types of catalysts supported on magnesium halides. The copolymers obtained in this manner have elasto-plastic properties, but are not heat resistant, since they have a relatively low melting point (around 100-130 °C).

EP-A-086 300, EP-A-170 255 and EP-A-145 368 relate to so called "impact polypropylene compositions" and describe polypropylene block copolymers having improved impact resistance and high stiffness, i.e. a flexural modulus higher than that of the inventive polypropylene compositions.

USP 4,489,195 describes the preparation of polyolefin thermoplastic elastomers in two stages of polymerization using stereospecific catalysts supported on magnesium halides; in the first stage homopolymer polypropylene is formed, and in the second, carried out preferably in gas phase, an elastomeric ethylene/propylene copolymer.

In order to prevent agglomeration of the particles, the temperature in the second stage is kept relatively low (under 50 °C). The polymer is obtained in powder form.

The need to operate at a relatively low temperature in the rubber copolymer formation stage penalizes the process from the point of view of the thermal exchange as well as the diminished productivity of the catalyst. According to the data furnished in the patent, the compositions do not include ethylene polymeric fractions insoluble in xylene at room temperature.

USP 4,491,652 describes the preparation of polypropylene thermoplastic elastomers in two stages, where in the first stage the propylene is polymerized to homopolymer polypropylene, and in the second one mixtures of ethylene-propylene are polymerized to form rubbery copolymers. The second stage is carried out in the presence of a solvent at temperatures of 60 °-80 °C. Operating at this temperature, one obtains partial dissolution of the rubbery copolymer with the formation of lumps which must then be disintegrated. According to the patent the disintegration is done by grinding. As a matter of fact, it is known that when the percentage of the rubbery ethylene-propylene copolymer exceeds about 20% of the total polymer, it is impossible to avoid the agglomeration of the particles even when the operation takes place in the presence of stereospecific catalysts (see European published patent application 0029651 and Belgian patent 876,413).

The agglomeration phenomenon is particularly critical when the ethylene-propylene copolymerization stage is done in gas phase. The fouling of the reactors prevents in practice to carry out the process in gas phase.

Now unexpectedly it has been found that using specific catalysts supported on magnesium chloride it is possible to obtain, even with processes in gas phase, polypropylene compositions with plasto-elastic properties, in the form of spheroidal particles having flowability and bulk density characteristics sufficiently elevated and such as to allow the use of same in normal processes of transformation to products without having to resort to preliminary granulation operations.

The compositions, as a result of their plasto-elastic characteristics, are suitable for all applications foreseen for traditional thermoplastic polyolefin elastomers.

Moreover, since the compositions are obtained under conditions where the rubbery phase which is formed is distributed uniformly in the polypropylene matrix, they provide properties superior to the corresponding compositions obtained by mechanical mixing of components.

Finally, since the compositions are obtained with very highly active catalysts, the amount of catalyst residue in said compositions is so small that the removal of catalysts residues is not necessary.

The compositions of the invention include:

A) 10-60 parts by weight, preferably 20-50 parts by weight, of homopolymer polypropylene with isotactic index greater than 90, preferably between 95 and 98, or of a crystalline propylene copolymer with ethylene and/or an alpha olefin  $\text{CH}_2 = \text{CHR}$ , where R is a 2-6 carbon alkyl radical, containing more than 85% by weight of propylene and having an isotactic index greater than 85;

B) 10-40 parts by weight of a polymeric fraction containing ethylene, insoluble in xylene at room temperature;

C) 30-60 parts by weight, preferably 30-50 parts by weight, of an amorphous ethylene-propylene copolymer fraction, optionally containing small proportions of a diene, soluble in xylene at room temperature and containing 40-70% by weight of ethylene.

The total content of the polymerized ethylene is between 20 and 60% by weight.

The molecular weight of the various fractions (determined by measuring intrinsic viscosity in tetrahydronaphthalene at 135°C) varies depending on the nature of the components and the melt index of the final product. It is comprised within the following preferred limits:

- 0.5 - 3 dl/g for fraction A);
- 2 - 8 dl/g for fractions B) plus C).

As already indicated the compositions are obtained in the form of spheroidal particles having an average diameter between 500 and 7000  $\mu\text{m}$  flowability (at 70°C) lower than 30 seconds; bulk density (tamped) greater than 0.4 g/cm<sup>3</sup>, in particular between 0.4 and 0.6 g/cm<sup>3</sup>.

The compositions present at least one melting peak determined at DSC at temperatures higher than 140°C; flex modulus lower than 700 MPa, preferably between 200 and 500 MPa; VICAT softening point greater than 50°C; Shore A hardness greater than 80 and Shore D hardness greater than 30; tension set at 75% lower than 60%, in particular between 20 and 50%; tensile stress greater than 6 MPa, in particular between 8 and 20 MPa.

The examination of the compositions under electronic microscope indicates that the phase dispersed is constituted by amorphous ethylene-propylene copolymer and has an average particle size smaller than 2  $\mu\text{m}$ .

The manufactured articles that can be obtained from the compositions find application particularly in the automotive, electrical cables and sporting goods fields.

The compositions are prepared by a polymerisation process including at least two stages, where in the first stage the propylene is polymerized to form component A), and in the following stages the ethylene-propylene mixtures are polymerized to form components B) and C).

The operation takes place in liquid or gas phase, or in liquid-gas phase.

A preferred process consists in carrying out the propylene homopolymerization stage using as a diluent the liquid propylene, and the copolymerization stage of the propylene and ethylene in gas phase without intermediate stages except for the partial degassing of the propylene.

The polymerization of the propylene may be done in the presence of ethylene or an alpha olefin such as butene-1, pentene-1, 4-methylpentene-1, in such quantities that the isotactic index of the resulting product is greater than 85%.

The copolymerization of the propylene and the ethylene can also occur in the presence of another alpha-olefin or a diene, conjugated or not, such as butadiene, 1,4-hexadiene, 1,5-hexadiene, ethylidene-norbornene-1.

The reaction temperature in the propylene polymerization stage and in the propylene and ethylene copolymerization stage may be equal or different, and is comprised generally between 40°C and 90°C, preferably 50-80°C in case of homopolymerization and 50-70°C in case of copolymerization.

The pressure of the first stage is the one that competes with vapor pressure of the liquid propylene at the working temperature, possibly modified by the vapor pressure of the small quantity of inert diluent used to feed the catalytic mixture and the hydrogen overpressure as regulator of the molecular weight.

The pressure relative to the copolymerization stage, if done in gas phase, can be between  $5.065 \cdot 10^5$  and  $30.39 \cdot 10^5$  Pa (5 and 30 atm). The stay time relative to the two stages vary depending on the desired rapport between the homopolymer fraction and the bipolymer B and C ones, and are generally between 30 minutes and 8 hours. Known traditional chain transfer agents, such as hydrogen and  $\text{ZnEt}_2$ , can be used as molecular weight regulators.

The catalyst used in the polymerization includes the reaction product of a solid compound containing a titanium compound and an electron-donor compound (internal donor) supported on magnesium chloride, with an Al-trialkyl compound and an electron-donor compound (external donor).

In order to obtain the compositions of the invention in the form of flowable particles, having high bulk density, it is critical that the solid catalyst component presents the following properties:

- surface area smaller than 100 m<sup>2</sup>/g, in particular between 50 and 80 m<sup>2</sup>/g;
- porosity: between 0.25 and 0.4 cm<sup>3</sup>/g;
- X-ray spectrum: presence of a halo at angles  $2\theta$  between 33.5° and 35° and no reflections at  $2\theta = 14.95^\circ$ .

The catalyst component is prepared following the method described below.

A magnesium chloride adduct with alcohol containing generally 3 moles of alcohol for mole of MgCl<sub>2</sub>, is obtained in the form of spherical particles by emulsifying the molten adduct in an inert hydrocarbon liquid immiscible with the adduct, and then cooling the emulsion very quickly in order to cause the adduct to solidify in spherical particle form.

The particles are then submitted to partial dealcoholization with a heating cycle between 50° and 130° C which brings the alcohol content from 3 to 1-1.5 moles per mole of MgCl<sub>2</sub>.

The adduct is then suspended in TiCl<sub>4</sub> cold, in a concentration of 40-50 g/l and consequently brought to a temperature of 80°-135° C at which it is maintained for a period of 1-2 h.

To the TiCl<sub>4</sub> is also added an electron-donor compound selected preferably among the alkyl, cycloalkyl or aryl phthalates such as for instance diisobutyl, di-n-butyl and di-n-octyl phthalate.

The excess of TiCl<sub>4</sub> is separated hot through filtration or sedimentation, and the treatment with TiCl<sub>4</sub> is repeated one or more times; the solid is then washed with heptane or hexane and dried.

The catalyst component thus obtained presents the following characteristics:

- surface area: less than 100 m<sup>2</sup>/g, in particular between 50 and 80 m<sup>2</sup>/g;
- porosity: 0.25 - 0.4 cm<sup>3</sup>/g;
- pores volume distribution such that more than 50% of the pores have a radius greater than 10 nm (100 Å);
- X-ray spectrum presenting a halo with maximum intensity between angles of  $2\theta$  of 33.5° and 35°, and where no reflection is present at  $2\theta$  of 14.95°.

The catalyst is obtained by mixing the catalyst component with an Al-trialkyl compound, preferably Al-triethyl and Al-triisobutyl, and an electron-donor compound selected preferably among silane compounds of the formula R'R''Si(OR)<sub>2</sub> where R' and R'', equal or different, are alkyl, cycloalkyl or aryl radicals containing 1-18 carbon atoms, and R is a 1-4 carbon alkyl radical.

Typical silanes are diphenyldimethoxysilane, dicyclohexyldimethoxysilane, methyl-tert-butyldimethoxysilane and diisopropyldimethoxysilane.

Silane compounds such as phenyltriethoxysilane can also be used.

The Al/Ti ratio is usually between 10 and 200 and the silane/Al molar ratio between 1/5 and 1/50.

The catalysts may be precontacted with small quantities of olefin (prepolymerisation), maintaining the catalyst in suspension in a hydrocarbon solvent and polymerizing at a temperature between room temperature and 60° C, and producing a quantity of polymer from 0.5 to 3 times the weight of the catalyst.

The operation can occur in liquid monomer also, producing in this case a quantity of polymer up to 1000 times the catalyst weight.

The data reported in the examples and text relative to the properties listed below have been determined by using the following methods:

| <u>Properties</u>              | <u>Method</u>                           |
|--------------------------------|---|
| 5 - Fluidity index (M.F.R.L.)  | ASTM-D 1238                             |
| - Ethylene percent by weight   | Spectroscopy I.R.                       |
| 10 - Intrinsic viscosity       | Determined in tetralene at<br>135°C     |
| - Xylene soluble %wt           | (see note preceding the<br>15 examples) |
| - Flex modulus                 | ASTM - D 790                            |
| 20 - Notched IZOD resilience   | ASTM - D 256                            |
| - VICAT (1 kg) softening point | ASTM - D 1525                           |
| - A/D Shore hardness           | ASTM - D 2240                           |
| 25 - Tension set at 75%        | ASTM - D 412                            |

|    |                        |  |
|----|------------------------|--|
|    | - Tensile stress       | ASTM - D 638   |
|    | - Surface area         | B.E.T.   |
| 5  | - Porosity             | B.E.T.   |
|    | - Bulk density         | DIN - 53194  |
| 10 | - Flowability          | The time it takes 100 g of<br>polymer to flow thorough a<br>funnel, whose output<br>opening has a diameter of<br>1.27 cm, and walls inclined<br>at 20° with respect to the<br>vertical.  |
| 15 |                        |  |
| 20 |                        |  |
| 25 | - Granulometry         | ASTM - D 1921 - 63   |
|    | - Whitening resistance | Determined by submitting to<br>impact disks of the polymer<br>being tested, obtained by<br>pressure-injection, with a<br>ram consisting of a<br>hemispheric punch with a<br>diameter of 12.7 mm and<br>weighing 78 g. Both the<br>minimum height to obtain<br>the whitening (h), and the |
| 30 |                        |  |
| 35 |                        |  |
| 40 |                        |  |
| 45 |                        |  |
| 50 |                        |  |
| 55 |                        |  |

size of the whitening area  
at the maximum height  
allowed by the apparatus  
(76 cm) are measured.

10

The samples to be submitted to the various physico-mechanical tests have been molded directly from the in polymer in the form of spherical particles, previously stabilized with 0.1% by weight of IRGANOX<sup>R</sup> 1010 and 0.1% by weight of BHT (2,6-di-tert-butyl-paracresol), under the following conditions and using a GBF V160 injection press:

- 15
- temperature of the melt polymer: 190 °C;
  - mold temperature 60 °C;
  - injection time 20 seconds;
  - cooling time 25 seconds.

20 The percentage by weight of total bipolymer (% Bp = % C + % B) is calculated by determining the weight of the propylene-ethylene mixture fed in the second stage and comparing it to the weight of the final product.

The weight percentages of the three fractions A, B and C, described in the text, are determined in the following manner:

25 
$$\%A = 100 - \%Bp$$

$$\%C = S_c - P \cdot Sp$$

30 where  $S_c$  and  $Sp$  are the percentage by weight of the xylene soluble portion of the final product and of the polypropylene fraction A respectively;  $P$  is the weight ratio between said fraction and the final product.

$$\%B = 100 - \%A = \%C.$$

35 The percentage by weight of ethylene contained in copolymer fraction C soluble in xylene has been calculated with the following formula:

$$C_F - C_P \cdot Q$$

40

$$\% \text{ Ethylene in fraction C} = \frac{\text{-----}}{\text{Y}}$$

Y

45

where

- 50
- $C_F$  = %wt. ethylene in the soluble in xylene of the final product;
  - $C_P$  = %wt. ethylene in the soluble in xylene of polypropylene fraction A;
  - $Q$  = %wt. soluble in xylene of fraction A multiplied by the weight fraction of A compared to the final product and divided by the weight fraction of the soluble in xylene of the final product.
  - $Y$  = %wt of C multiplied by %wt of total bipolymer, divided by one hundred.

#### Note

#### 55 DETERMINATION OF THE PERCENTAGE SOLUBLE IN XYLENE

2.5 g of polymer are dissolved in 250 ml of xylene at 135 °C under agitation. After 20 minutes the solution is left to cool down to 25 °C, still agitating, and then left to rest for 30 minutes.

The precipitate is filtered with filter paper; the solution is evaporated in nitrogen current and the residual under vacuum dried at 80 °C until it reaches constant weight. In this manner the percentage by weight of polymer soluble in xylene at room temperature is calculated. The percentage by weight of polymer insoluble in xylene at room temperature is considered as the isotactic index of the polymer. The value thus obtained coincides substantially with the isotactic index determined via extraction with boiling n-heptane, which by definition constitutes the isotactic index of the polypropylene.

## EXAMPLES

### 10 GENERAL OPERATING METHODS

The test have been conducted in a 22 l stainless steel autoclave, with helical magnetic agitator operating at about 90 rpm.

Temperature and pressure are kept constant during reaction unless otherwise indicated.

15 The gas phase is continuously analyzed with a processing gas-chromatograph.

The operation is a batch operation in two stages: the first stage consists of the homopolymerization of the propylene in liquid monomer, the second one of the copolymerization of ethylene and propylene in gas phase.

A) 1st stage.

20 In the autoclave are introduced at 20 °C in order:

16 l of liquid propylene and the catalytic complex, constituted by a solid component (about 0.15 g) and a mixture of 75 ml of Al-triethyl (TEAL) at 10% in hexane and an adequate quantity of phenyltriethoxysilane (PES) - (molar ratio Al/PES = 10).

25 The catalytic system is fed with propylene pressure. The temperature is brought to 70 °C in about 10 minutes and kept constant for the entire period of the polymerization. The hydrogen is analyzed continuously in gas phase and fed in order to maintain constant the desired concentration.

Whenever ethylene is used as a comonomer, an adequate quantity of this olefin is fed continuously in order to maintain constant the percentage in gas phase.

30 After the established time, practically all the remaining monomer is eliminated by degassing at 60 °C at atmospheric pressure.

B) 2nd stage.

The homopolymer from the first stage, after having taken a sample for the various analyses, is brought to the established temperature. Consequently are fed in order propylene and ethylene in the ratio a quantity desired in order to obtain the set gas phase composition and pressure.

35 During polymerization the pressure is maintained constant by feeding an ethylene-propylene mixture having the same composition as the desired bipolymer and contained in a cylinder with a thermostat at 90 °C.

The duration of the feeding vary according to the reaction of the catalytic system and the quantity of the bipolymer needed to supply the planned relative homo- and bipolymer composition. At the end of the test the powder is discharged, stabilized and oven dried in nitrogen current at 60 °C. The catalyst component used is prepared from a  $\text{MgCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$  adduct obtained in the form of spherical particles, following the method in example 2 of US patent 4,399,054, but operating at 3,000 rpm instead of 10,000 rpm. The adduct is then dealcoholized by heating at gradually increasing temperature from 50 ° to 100 °C in nitrogen current until the alcohol content reaches 1.5 moles per mole of  $\text{MgCl}_2$ .

45 The partially dealcoholized adduct has a surface area = 9.1 m<sup>2</sup>/g; bulk density = 0.564 g/cm<sup>3</sup>.

25 g of said adduct are added to 625 ml of  $\text{TiCl}_4$  under agitation at 0 °C.

It is heated to 100 °C in 1 hr. When the temperature reaches 40 °C, diisobutylphthalate is added in molar ratio  $\text{Mg}/\text{diisobutylphthalate} = 8$ . It is heated to 100 °C for 2 hours, left to settle and then the liquid is syphoned hot. 550 ml of  $\text{TiCl}_4$  are introduced and heated at 120 °C for 1 h. It is left to settle and then the liquid is syphoned hot. The solid is washed 6 times using 200 ml of anhydrous hexane at 60 °C, and then 3 times at room temperature. The solid, after having been under vacuum dried, presents the following characteristics:

- porosity = 0.261 cm<sup>3</sup>/g;
- surface area = 66.5 m<sup>2</sup>/g;
- bulk density = 0.440 g/cm<sup>3</sup>.

All the tests carried out and the relative operating conditions are reported on Tables 1A and 1B.

In examples 2 and 4 was used, as external donor, diphenyldimethoxysilane instead of phenyltriethoxysilane.



Table 1A

| Examples                                      | 1     | 2     | 3     | 4     |
|---|-------|-------|-------|-------|
| <b>1st PHASE</b>                              |       |       |       |       |
| - Pressure Ate                                | 36.4  | 30.4  | 35.6  | 31.2  |
| - Time min.                                   | 90    | 60    | 30    | 60    |
| - H <sub>2</sub> in gas phase %moles          | 14.1  | 0.6   | 11.9  | 1.7   |
| - C <sub>2</sub> in gas phase %moles          | -     | -     | -     | 1.55  |
| - Isotactic index % wt.                       | 94.6  | 95.8  | 95.2  | 94.7  |
| - Intrinsic viscosity dl/g                    | 0.68  | 1.98  | 0.96  | 1.36  |
| - Ethylene % wt.                              | -     | -     | -     | 2.6   |
| - Ethylene in portion soluble in xylene % wt. | -     | -     | -     | 12.1  |
| <b>2nd PHASE</b>                              |       |       |       |       |
| - Temperature °C                              | 60.0  | 70    | 60    | 70    |
| - Pressure Ate                                | 12.0  | 11.3  | 11.3  | 11.3  |
| - Time min.                                   | 215   | 350   | 370   | 405   |
| - H <sub>2</sub> in gas phase %moles          | 0.4   | 1.0   | 2.05  | 1.1   |
| - C <sub>2</sub> in gas phase %moles          | 29.1  | 35.2  | 51.1  | 33.9  |
| - C2/C3 in feeding mixture wt/wt              | 45/55 | 55/45 | 70/30 | 51/49 |

Table 1B

| Examples  | 1    | 2     | 3    | 4    |
|---|------|-------|------|------|
| <b>FINAL PRODUCT</b>                                  |      |       |      |      |
| - Yield Kg pol./gTi                                   | 851  | 1230  | 933  | 1380 |
| - Bipolymer (Bp) % wt                                 | 56.3 | 76.4  | 78.2 | 57.4 |
| - Ethylene % wt                                       | 30.1 | 41.5  | 55.1 | 29.3 |
| - Intrinsic viscosity dl/g                            | 1.89 | 2.38  | 2.44 | 1.95 |
| - Fluidity index g/10'                                | 18.0 | 1.25  | 2.7  | 4.0  |
| - Xylene soluble portion (S <sub>c</sub> ) % wt       | 42.5 | 42.7  | 44.2 | 36.5 |
| - Fraction B % wt                                     | 16.2 | 34.8  | 38.0 | 21.8 |
| - Fraction C % wt                                     | 40.1 | 41.6  | 40.2 | 35.6 |
| - C2 in xylene soluble portion (C <sub>f</sub> ) % wt | 42.5 | 52.1  | 58.8 | 44.8 |
| - C2 in fraction C % wt                               | 45.0 | 53.3  | 67.5 | 47.1 |
| - Melt point (DSC) °C                                 | 163  | 163.5 | 163  | 148  |
| - Flex modulus MPa                                    | 350  | 320   | 270  | 300  |
| - Notched IZOD resilience (c.i.) -40 J/m              | N.B. | N.B.  | 950  | N.B. |
| - Whitening resistance (height) cm                    | >76  | >76   | >76  | >76  |
| - Whitening resistance (area) cm <sup>2</sup>         | 0    | 0     | 0    | 0    |
| - Vicat (1 Kg) °C                                     | 84   | 86    | 73   | 97   |
| - SHORE A hardness                                    | 97   | 94    | 91   | 95   |
| - SHORE D hardness                                    | 45   | 42    | 36   | 46   |
| - Tension set at 75% %                                | 48   | 40    | 37   | 40   |
| - Tensile stress (tract.) MPa                         | 8.1  | 12.1  | 11.7 | 15.6 |
| - Tamped bulk density Kg/l                            | 0.47 | 0.46  | 0.48 | 0.47 |
| - Flowability at 70 °C sec.                           | 11   | 11    | 12   | 14   |
| - Granule average diam. um                            | 1400 | 2000  | 1400 | 2000 |
| N.B. = "not broken"                                   |      |       |      |      |

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosure. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of

these embodiments can be effected without departing from the spirit and scope of the invention and described and claimed.

# Claims

- 5 1. A polypropylene composition comprising:
  - A) 10-60 parts by weight of homopolymer polypropylene with isotactic index greater than 90, or crystalline propylene copolymer with ethylene and/or with a  $\text{CH}_2=\text{CHR}$  olefin where R is a 2-6 carbon alkyl radical, containing over 85% by weight of propylene and having an isotactic index greater than 85;
  - 10 B) 10-40 parts by weight of a crystalline polymer fraction containing ethylene, insoluble in xylene at room temperature;
  - C) 30-60 parts by weight, of an amorphous ethylene-propylene copolymer fraction containing optionally small proportions of a diene, soluble in xylene at room temperature and containing from 15 40 to 70% by weight of ethylene;
 said composition having a flex modulus smaller than 700 MPa, tension set at 75% less than 60%, tensile stress greater than 6 MPa and notched IZOD resilience at  $-20^\circ$  and  $-40^\circ\text{C}$  greater than 600 J/m.
- 20 2. The composition of claim 1 where the total content of polymerized ethylene is between 20 and 60% by weight.
3. The composition of claim 1 or 2 where the flex modulus is between 200 and 500 MPa, the tension set between 20 and 50%, and the tensile stress between 8 and 20 MPa.
- 25 4. The composition of claim 1 in the form of spheroidal particles with average diameter between 500 and 7000  $\mu\text{m}$ , flowability less than 30 seconds and tamped bulk density greater than 0.4  $\text{g}/\text{cm}^3$ .
5. A process for the preparation of the composition of claim 1, comprising a polymerization stage of the propylene, or its mixtures with ethylene and/or alpha olefins, to form polymer phase A), and one or more stages of polymerization of ethylene-propylene mixtures containing optionally a diene to form polymer phases B) and C), using catalysts obtained from an Al-trialkyl compound and a solid component comprising an halide or halogen-alcoholate of Ti and an electron-donor compound supported on anhydrous magnesium chloride, said component having a surface area smaller than 100  $\text{m}^2/\text{g}$ , porosity between 0.2 and 0.4  $\text{cm}^3/\text{g}$ , pore volume distribution such that over 50% of the pores have a radius greater than 10 nm (100 Å), and presenting an X-ray spectrum with a halo with maximum intensity between angles  $2\theta$  of  $33.5^\circ$  and  $35^\circ$  and showing no reflections at  $2\theta$  of  $14.95^\circ$ .
- 30 6. The process of claim 5, where the propylene polymerization stage is carried out in liquid monomer, and the stage, or stages, of ethylene-propylene copolymerization are carried out in gas phase.
7. The process of claim 5 carried out in gas phase.
8. A manufactured article obtained from the composition of claim 1.

# Patentansprüche

1. Polypropylenzusammensetzung, umfassend
  - (A) 10 bis 60 Gew.Teile von homopolymerem Polypropylen mit einem Isotaktizitätsindex voll größer als 90 oder kristallinem Propylen-Copolymeren mit Ethylen und/oder mit einem  $\text{CH}_2=\text{CHR}$ -Olefin, worin R für einen  $\text{C}_{2-6}$ -Alkylrest steht, das mehr als 85 Gew.% Propylen enthält und einen Isotaktizitätsindex von größer als 85 besitzt;
  - 50 (B) 10 bis 40 Gew.Teile einer Ethylen enthaltenden, kristallinen Polymerfraktion, die in Xylol bei Raumtemperatur unlöslich ist;
  - 55 (C) 30 bis 60 Gew.Teile einer amorphen Ethylen-Propylen-Copolymerfraktion, die gegebenenfalls geringe Anteile eines Diens enthält, in Xylol bei Raumtemperatur löslich ist und 40 bis 70 Gew.% Ethylen enthält;
 wobei diese Zusammensetzung einen Biegemodul von geringer als 700 MPa, eine bleibende Verfor-

mung bei 75% von geringer als 60%, eine Zugspannung von größer als 6 MPa und eine gekerbte Izod-Rückprallelastizität bei -20 bis -40 °C von größer als 600 J/m besitzt.

2. Zusammensetzung gemäß Anspruch 1, worin der Gesamtgehalt an polymerisiertem Ethylen zwischen 20 und 60 Gew.% beträgt.
3. Zusammensetzung gemäß Anspruch 1 oder 2, worin der Biegemodul zwischen 200 und 500 MPa, die bleibende Verformung zwischen 20 und 50% und die Zugspannung zwischen 8 und 20 MPa beträgt.
4. Zusammensetzung gemäß Anspruch 1, in Form von sphäroidischen Teilchen mit einem durchschnittlichen Durchmesser zwischen 500 und 7000  $\mu\text{m}$ , einer Fließfähigkeit von geringer als 30 Sekunden und einer gestampften Schüttdichte von größer als 0,4 g/cm<sup>3</sup>.
5. Verfahren zur Herstellung der Zusammensetzung von Anspruch 1, umfassend eine Polymerisationsstufe von Propylen oder seinen Mischungen mit Ethylen und/oder  $\alpha$ -Olefinen zur Bildung einer polymeren Phase (A) und eine oder mehrere Polymerisationsstufen von Ethylen-Propylen-Mischungen, gegebenenfalls enthaltend ein Dien zur Bildung von polymeren Phasen (B) und (C) unter Verwendung von Katalysatoren, erhalten aus einer Al-trialkylverbindung und einer festen Komponente, umfassend ein Halogenid oder Halogenalkoholat von Ti und eine Elektronen-Donorverbindung, trägergestützt auf wasserfreiem Magnesiumchlorid, wobei diese Komponente eine spezifische Oberfläche von geringer als 100 m<sup>2</sup>/g besitzt, eine Porosität zwischen 0,2 und 0,4 cm<sup>3</sup>/g, eine Porenvolumenverteilung derart, daß über 50% Poren einen Radius von größer als 10 nm (100 Å) aufweisen, und ein Röntgenspektrum aufweist mit einem Halo mit maximaler Intensität zwischen Winkeln  $2\theta$  von 33,5° und 35°, das keine Reflexionen bei  $2\theta$  von 14,95° aufweist.
6. Verfahren gemäß Anspruch 5, worin die Propylen-Polymerisationsstufe in flüssigem Monomeren durchgeführt wird und die Stufe oder Stufen der EThylen-Propylen-Copolymerisation in der Gasphase durchgeführt werden.
7. Verfahren gemäß Anspruch 5, durchgeführt in der Gasphase.
8. Erzeugnis, hergestellt aus der Zusammensetzung von Anspruch 1.

#### Revendications

1. Une composition de polypropylène comprenant:
  - A) 10 à 60 parties en poids d'un homopolymère de propylène présentant un indice isostatique supérieur à 90, ou d'un copolymère de propylène cristallin avec de l'éthylène et/ou avec une oléfine de formule  $\text{CH}_2=\text{CHR}$ , dans laquelle R représente un radical alkyle comportant 2 à 6 atomes de carbone, contenant plus de 85% en poids de propylène et présentant un indice isostatique supérieur à 85;
  - B) 10 à 40 parties en poids d'une fraction de polymère cristallin contenant de l'éthylène, insoluble dans le xylène à la température ambiante;
  - C) 10 à 60 parties en poids d'une fraction de copolymère éthylène propylène amorphe contenant éventuellement de petites quantités d'un diène, soluble dans le xylène à la température ambiante et contenant de 40 à 60% en poids d'éthylène;
 la dite composition présentant un module de flexion inférieur à 700 MPa, une déformation rémanente après allongement de 75% inférieure à 60%, une contrainte de traction supérieure à 6 MPa et une résilience Izod sur éprouvette entaillée à -20 °C et -40 °C supérieure à 600 J/m.
2. La composition selon la revendication 1, dans laquelle la teneur totale d'éthylène polymérisé est de 20 à 60% en poids.
3. La composition selon la revendication 1 ou 2, dans laquelle le module de flexion est compris entre 200 et 500 MPa, la déformation rémanente après allongement est comprise entre 20 et 50% et la contrainte de traction est comprise entre 8 et 20 MPa.

4. La composition selon la revendication 1, sous la forme de particules sphéroïdales présentant un diamètre moyen compris entre 500 et 7000  $\mu\text{m}$ , une capacité d'écoulement inférieure à 30 secondes et une densité apparente tassée supérieure à 0,4  $\text{g}/\text{cm}^3$ .
5. Un procédé pour la préparation d'une composition selon la revendication 1, comprenant une étape de polymérisation du propylène, ou de ses mélanges, avec de l'éthylène et/ou des  $\alpha$ -oléfinés, pour former une phase de polymère (A), et une ou plusieurs étapes de polymérisation de mélanges xylène-propylène contenant éventuellement un diène pour former les phases de polymère (B) et (C), en utilisant des catalyseurs obtenus à partir d'un dérivé de trialkylaluminium et d'un composant solide comprenant un halogénure ou un halogéno-alcoolate de Ti et un composé électrodonneur supporté sur du chlorure de magnésium anhydre, ledit composant présentant une surface spécifique inférieure à 100  $\text{m}^2/\text{g}$ , une porosité comprise entre 0,2 à 0,4  $\text{cm}^3/\text{g}$ , une distribution de volume de pores telle que plus de 50% des pores présentent un rayon supérieur à 10 nanomètres (100 angstroms), et présentant un spectre aux rayons X présentant un halo d'une intensité maximale entre les angles  $2\theta$  de 33,5° et 35° et ne présentant aucune réflexion à un angle  $2\theta$  de 14,95°.
6. Le procédé selon la revendication 5, dans lequel l'étape de polymérisation du propylène est mise en oeuvre dans un monomère liquide et l'étape ou les étapes de copolymérisation de l'éthylène-propylène sont mises en oeuvre en phase gazeuse.
7. Le procédé selon la revendication 5, mis en oeuvre en phase gazeuse.
8. Un article manufacturé préparé à partir de la composition selon la revendication 1.